

ON THE THEORY OF
ONE-ELECTRON SPECTRAL WEIGHT FUNCTIONS
AND
X-RAY PHOTOEMISSION

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- A. Vertex correction calculations for an electron gas, J. Phys. C 7 (1974) p. 3013
- B. Aspects on diagrammatic expansion for models related to a homogeneous electron gas, J. Phys. C 8 (1975) p. 1535
- C. Exact numerical solutions of a Nozières-de Dominicis type model problem, Phys. Lett. 56 A No 4 (1976)



INTRODUCTION

The Bohr model of an atom resembles a miniature planetary system, where the planets-electrons are orbiting around the sun-nucleus, being held together by forces which are proportional to the inverse squares of the distance between the constituents. In this microcosmos the interaction comes from the electrical Coulomb force ($\propto e^2/r^2$) which is repulsive between two electrons and attractive between an electron and a nucleus.

From the microscopic point of view a solid consists of an extremely large number of atoms (of the order of 10^{23}). A first principle calculation in the sense of keeping track of all the movements of such an immense number of constituents is not possible. Despite this, however, one would like to understand experimental facts from the microscopic point of view. The many-body-theory applied to solid-state physics has had a great success in this respect during the last two decades. The development of fast computers has made more and more realistic calculations possible. The major difficulty, when trying to correlate the microscopic view with experimental results, is to find useful approximation schemes, i.e. to find mathematically reasonable and physically plausible simplifications which will make it possible to carry out explicit calculations of particular properties.

A simple metal may be viewed in the following way: when atoms are brought together to form a piece of metal, the most loosely-bound electrons of each atom, on coming close to all the other atoms, will not know where they originally belonged. Hence these electrons

will float around in the metal. This class of electrons in a metal are called conduction electrons. The rest of the atoms stripped of their most loosely-bound electrons will, however, sit in specific positions forming a well-defined array of metal ions. The electrons tied to metal ions in this way are called core-electrons.

The array of metal ions will in ideal metals consist of an infinite repetition of identical structural parts. This means that the conduction electrons "see" a periodic potential. However, in problems in which the important physics comes from the dynamical properties of the conduction electrons, one may for some metals neglect the periodic potential (these are the so-called free-electron-like metals). As far as the conduction electron is concerned the metal ions then merely act as a positive compensating background-charge which could as well have been homogeneously smeared out. Thus one may expect that some properties of the metal connected with the conduction electrons could be understood from a model in which the conduction electrons move in a homogeneous positive background. This model of an "interacting electron gas" has been successful when describing properties of simple metals e.g. sodium, magnesium, aluminum, and potassium. It is used in the present dissertation.

Many-body-theory uses a rather abstract language with concepts like Feynman diagrams, Green's functions, and spectral functions. The spectral function A related to the one-electron Green's function

($A(k) = \frac{1}{\pi} \cdot |\text{Im } G(k)|$) is a key quantity in the present dissertation and it is directly related to the results of a number of experiments, (see e.g. summary of paper C). The spectral function describes the one-electron properties of the system or expressed in other words describes what happens to a system of interacting electrons when one electron is injected or extracted.

The present dissertation is concerned with approximation schemes for calculating the one-electron spectral functions of an interacting electron gas (papers A and B) and with an explicit model calculation of a one-electron spectral function in connection with the XPS-problem. XPS stands for x-ray photoemission which occurs when a core-electron is suddenly knocked out of the metal by an x-ray quantum coming from an external source.

SUMMARY OF PAPER A

The one-electron Green's function $G(k)$ for an electron gas may be formally given as the solution of a coupled set of integral equations (eqs. 1a-1e). One would then like to have available a systematic approximation scheme to make possible the extraction of explicit information from this set of equations. One way is to expand the self-energy $\Sigma(k)$ to a given order in the screened interaction and then use the Dyson equation to obtain an approximate solution for $G(k)$. Successful calculations have been carried out, expanding to first order in the screened interaction (see ref. Hedin and Lundqvist 1969 for a review). The present paper describes a straightforward

extension to second order in the screened interaction. The amount of useful information on the electron gas obtained in this second order calculation is limited by the fact that the resulting spectral functions violate the condition of being positive for all frequencies. However, the calculation gives information on the approximation scheme as such, casts doubts on some predictions based on first-order theory, and suggests that alternative systematic and feasible approximation schemes are needed.

SUMMARY OF PAPER B

An attempt is made to infer how various approximation schemes for obtaining one-electron Green's functions work when applied to different model problems connected with the interacting electron gas. The similarity between a model of an electron gas and a model of a core-electron coupled to an electron gas is discussed in this respect, and it is also suggested that the extraction of a conduction electron close to the bottom of the band affects the electron gas in approximately the same way as the creation of a core-hole. The various models serve as a testing ground for the approximation schemes. Especially the simplest of these models allows explicit calculations. Since it is possible to obtain the exact solution for this model the nature and merits of the approximation schemes can be demonstrated in this case. The relations between the models are discussed and it is concluded that the models are similar enough to make it plausible that the nature and merits of a given approximation scheme

will not depend on which of the models it is applied to. An iterative expansion method is developed which turns out to be especially favourable.

SUMMARY OF PAPER C

A new integral equation (eq.5) is found which applies to the spectral-weight function of a model for a core-electron coupled to a homogeneous electron gas. The spectral weight function for this model is easily obtained numerically from the integral equation. The emphasis in the paper is to make some connection with recent experimental observations of XPS-spectra (X-ray photoemission) for simple metals. The kinetic energy of the escaping photoelectrons coming from a certain atomic shell will not always have the same magnitude since the core-electrons in the metal will feel the presence of the conduction electrons and may during excitation by the x-ray quanta loose energy to the conduction electrons. The situation using quantum-mechanical language may be described as follows : The initial state consisting of the electron gas (i.e. the N conduction electrons) and a core electron is given by $|\psi_i\rangle = |c\rangle |N\rangle$ where $|c\rangle$ is the state vector of a core-electron with energy ϵ_c and $|N\rangle$ is the state vector of the electron gas in its ground-state. The final state, in which the core-electron has been knocked out of the metal by a photon of energy $\hbar\omega$, is $|\psi_f\rangle = |k\rangle |N^*,s\rangle$ where $|k\rangle$ is the state vector of an outgoing electron with energy ϵ_k and $|N^*,s\rangle$ is the state vector of the electron gas in the presence of a core-hole in an excited state s of energy ϵ_s . The probability, W , for the escaping photoelectron to have energy ϵ_k may be given by the Golden Rule expression

$$W \sim \sum_s |\langle N^*, s | N \rangle|^2 |p_{kc}|^2 \delta(\hbar\omega - \epsilon_k - \epsilon_s + \epsilon_c) \sim A(\hbar\omega - \epsilon_k + \epsilon_c) =$$

$$= \sum_s |\langle N^*, s | N \rangle|^2 \delta(\hbar\omega - \epsilon_k - \epsilon_s + \epsilon_c)$$

where the last proportionality comes from neglecting the weak k -dependence of the dipole matrix element p_{kc} . The spectral weight function, $A(\epsilon)$, is then a direct measure of the energy distribution of the escaping electrons. However, only the instantaneous (intrinsic) effect is taken into account. The core-electron may lose additional energy to the conducting electrons on its way out of the metal (extrinsic effects and surface effects). In a region starting from the edge, i.e. from the maximum photoelectron energy $\epsilon_{\max}$, the intrinsic effect may be supposed to dominate. The edge of the energy distribution is of great interest because many-body-theory has suggested that its shape should be dominated by a many-body effect which manifests itself in a power-law behaviour $1/(\epsilon_{\max} - \epsilon)^\alpha$ in the limit $\epsilon \rightarrow \epsilon_{\max}$, where ϵ is the energy parameter of the photoelectrons. Some of the conclusions drawn from and possible extensions suggested by the results of the present paper are:

1. The power-law behaviour is valid in a finite energy range of the order of the plasma frequency. This gives an a posteriori motivation for a recent method of extracting power-law-indices α (see ref. Citrin et al 1975).
2. The striking agreement of the power-law indices obtained in the present paper (despite its rather crude approach) with those obtained experimentally by Citrin et al (see the table below) indicates

that a model of the present type is very adequate in connection with the interpretation of XPS-spectra. This conclusion is also supported by the comparison between this model and the Nozières-de Dominicis model made in the paper.

3. The integral equation formulation may be used to include and to estimate other residual effects of the core-electron-conduction-electron-coupling in the same spirit.

4. The fact that $|\alpha(\omega) - \alpha(0)| \ll 1$ in a finite range may be a physical property of the electron gas, the origin of which if further explored might give some new insight into the electron gas problem.

α -values as obtained from the present calculations and extracted from experimental observations

	Na	Li	Mg	Al
α theory	.21	.24	.13	.11
α exp.	.20 ³⁾	.245 ²⁾	.13 ¹⁾	.115 ¹⁾

¹⁾ P.H. Citrin, G.K. Wertheim, and Y. Baer, Phys. Rev. Lett. 35 (1975) 885.

²⁾ Y. Baer, P.H. Citrin, and G.K. Wertheim (1976), to be published.

³⁾ P.H. Citrin, private communication.

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